Effect of Milling on the Densification of SiC-Based Composites from Polysilazane

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Abstract

High density SiC-based composites from polysilazane were fabricated by high energy milling and hot pressing. After cross-linking at 200 °C, the polysilazane was pyrolysed at 1000 °C in N₂ for 2 h to form amorphous Si-C-N-O followed by high energy milling for 1 h. Milled amorphous Si-C-N-O was sintered in hot pressing at 1600 and 1700 °C for 1 h in vacuum under the applied pressure of 50 MPa. Although no sintering additives were used, dense SiC-based composites were obtained with this method. Sintered density was 3.04 g/cm³, while only 2.57 g/cm³ for amorphous Si-C-N-O without milling. It is suggested that the liquid phase generated during the formation of Si₂N₂O facilitated the densification of the composite.

Keywords: high energy milling, polysilazane, SiC-based composites, Si₂N₂O

1. Introduction

It is well known that SiC-based composite has excellent mechanical and thermal properties at high temperature. However, SiC has a high covalent bonding and low-self diffusivity, making it difficult to obtain dense material with normal sintering technique. Hot pressing sintering with temperature and pressure at 2500 °C and 5 GPa, respectively, is needed to obtain dense SiC [1]. Another effort to obtain SiC at lower temperature is reported by Xie et al. [2]. They succeeded in fabricating SiC with 96% of theoretical density at 1300°C with an applied pressure of 4-4.5 GPa. However, these processes are not suitable for industrial application due to high processing temperature and/or pressure. To overcome this problem, normally sintering additives are used to fabricate dense SiC. Moreover, the addition of sintering additives also decreases the sintering temperature of SiC. In liquid phase sintering, sintering additives react with thin layer SiO₂ that exists on the surface of SiC to form a liquid phase and enhance the densification of SiC. Although the sintering additives can increase the density of SiC, the grain growth can be enhanced with the addition of sintering additives [3], which might decrease the mechanical properties of SiC.

Polysilazane, one of the polymer derived-ceramics, has been applied in wide range of applications, such as synthesis of fibers and coatings [4-9]. According to manufacturer [10], polysilazane can be derived to Si-based ceramics such as SiC, SiC/Si₃N₄ or Si₃N₄O₂ depend on the atmosphere of the pyrolysis. Nowadays, we can find a published report about fabrication of Si₃N₄ [11] or Si₃N₄/SiC [4,11-15] from polysilazane. However, to obtain fully dense ceramic composites from polysilazane, the sintering additives are still required [11-15]. Therefore, fabrication of SiC-based composites from polysilazane without the addition of sintering additives is still challenging.
In this study, we successfully fabricated high density SiC-based composites from polysilazane prepared by high energy milling without intentional addition of sintering additives. One hour of high energy milling using 0.45 mm ZrO$_2$ beads was performed for the milling of amorphous Si-C-N-O powder before sintering. It seems that the formation of Si$_2$N$_2$O in the sintered amorphous Si-C-N-O prepared by high energy milling played an important role in promoting densification. The phases generated during sintering, density, and microstructure of amorphous Si-C-N-O prepared by high energy milling were compared to amorphous Si-C-N-O without milling.

2. Experimental

Starting materials in this study were commercial polysilazane (KiON Ceraset Polysilazane 20, USA). Cross-linked polysilazane was obtained by heating at 200 °C for 90 min in hot plate followed by grinding in mortar and pestle. Cross-linked powder was pyrolysed at 1000 °C under N$_2$ atmosphere for 2 h to obtain amorphous Si-C-N-O powder. Although the pyrolysis was performed in N$_2$, atmosphere, oxygen element was found in the amorphous powder [9,15] with chemical composition of Si$_{1.00}$C$_{1.55}$N$_{0.81}$O$_{0.17}$ [15]. High energy milling (MiniCer, Netzch, Germany) was used to reduce the particle size of amorphous Si-C-N-O powder for 1 h using 0.45-mm ZrO$_2$ beads at 3000 rpm. Milled powders were put in the graphite die and hot-pressed (ThermVac Engineering Inc., Korea) at 1600 and 1700 °C for 1 h in vacuum under the applied pressure of 50 MPa. The samples were named HEM1600 and HEM1700 for high energy milling of amorphous Si-C-N-O sinter at 1600 and 1700 °C, respectively. For comparison, amorphous Si-C-N-O was hot-pressed at 1600 and 1700 °C at same condition without milling step, named 1600 and 1700, respectively.

The Archimedes principle was used to measure the density of the sintered specimens. The phases generated after sintering was analyzed by X-ray diffraction (XRD: X’Pert PRO MPD, PANalytical B.V., The Netherlands), using the Cu Kα line, 40 kV and 30 mA, and Rietveld refinement were performed for quantitative phase verification after sintering. The microstructures of specimens and composition were examined by scanning electron microscopy (SEM: Hitachi S-4800, Japan) equipped with an energy dispersive X-ray spectrometer (Horiba EX-250).

3. Results and discussion

Figure 1 shows the particle size of amorphous Si-C-N-O powders before and after milling process. The amorphous Si-C-N-O before milling had an irregular shape, as shown in Figure 1 (a). One hour of high energy milling resulted in size decrease to less than 1,000 nm, as shown in Figure 1 (b), while the shape of particle did not change significantly after milling.
impurity from milling media, which was inevitable. Since the amorphous powder composed of Si, C, N, and O, either SiO2, SiC or Si3N4 can be formed depending on sintering condition. Based on Gibbs free energy at 1600 °C, SiO2 has the lowest energy of -576.020 kJ mol\(^{-1}\) compared to Si3N4 (-37.868 kJ mol\(^{-1}\)) and SiC (-53.173 kJ mol\(^{-1}\)) [16]; hence, in the beginning of sintering the formation of SiO2 was favorable, which was confirmed in the XRD results as shown in Figure 2.

The formation of SiO2 along with Si3N4 led to the formation of Si2N2O follow the reaction equation (1) [17]:

\[
\text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{N}_2\text{O}
\]

It was reported that Si3N2O was only formed via liquid phase at the eutectic composition of 98 Si3N4-2 SiO2 mol % [17-18]. The greater amount of Si3N2O at 1700 °C than 1600 °C can be explained by the complete reaction between Si3N4 with SiO2, thus no SiO2 peaks could be observed at 1700 °C. One notable thing is the presence of β-Si3N4 without showing α-Si3N4. According to Tanaka et al. [19], the temperature of transformation α- to β- Si3N4 is 1750 °C, which is higher than this observation. In our case, the transformation of α- to β-Si3N4 was completed at <1600 °C. The lower α- to β-Si3N4 transformation temperature than the previous report might be attributed to the high-energy milling process as also reported in the case of lowering sintering temperature of Gd doped-Ceria [20].

Since β-Si3N4 is more energetically favorable than α-Si3N4 at high temperature, the transformation from α- to β-Si3N4 is irreversible. In contrast, no SiO2 peaks were observed at 1600 °C for hot-pressed amorphous Si-C-N-O without milling as seen in Figure 2. Therefore, as expected, the formation of Si3N2O did not occur without the presence of SiO2. It seemed either high energy milling or impurity ZrO2 might be affected to the formation of SiO2, as it occurred only in the milled amorphous Si-C-N-O. Only metastable α-SiC (2H) phase, α-Si3N4 and C were formed at 1600 °C.

At 1700 °C, all metastable α-SiC (2H) phase transformed to stable phase β-SiC and the decomposition of Si3N4 under the existence of free C [21] resulted in the excess Si.

Figure 3 shows the density of SiC-based composites with and without milling. Regardless of the milling process, the composite density increased with the increase of hot pressing temperature as shown in Figure 3. The densities of HEM1600 and HEM1700 were 2.80 and 3.04 g/cm\(^3\), respectively, and 1.53 and 2.47 g/cm\(^3\) for 1600 and 1700, respectively. There were two possibilities of liquid phase sintering mechanism in this study: the presence of ZrO2 impurity that acted as sintering additives or the formation of Si3N2O that involved liquid. One of the important things in the liquid phase sintering was that the additives should not react with SiC or Si3N4 during sintering [22] since the reaction between additive and the matrix hindered the formation of liquid phase [23]. There are few studies that have reported ZrO2 as sintering additives for Si3N4 [24-27], while the formation of ZrN was reported during sintering of Si3N4 with the addition of ZrO2 as sintering additives [24-25]. Moreover, fully dense Si3N4 could not reach even ZrO2 content which was increased up to 20 wt.% [27]. In order to investigate the effect of ZrO2 impurity in the composites, we added intentionally 5 wt.% and 10 wt.% of ZrO2 (mean particle size: 200 nm) to the amorphous Si-C-N-O and hot pressed at 1700 °C in the same condition. The densities were 2.04 g/cm\(^3\) and 2.21 g/cm\(^3\) for 5 wt.% and 10 wt.% addition of ZrO2, respectively. It seemed that the ZrO2 introduced by the high energy milling created almost no effect to enhance the densification of HEM1600 and HEM1700. Moreover, the amount of ZrO2 introduced by high energy milling was 3.2–3.4 wt. % based on the quantitative analysis of XRD, which meant that it was quite low to act as sintering additives. Therefore, enhancing sintering density of HEM1600 and HEM1700 might be explained with the existence of liquid phase associated with the formation of Si3N2O. This liquid phase acted as a high diffusivity path to enhance the density of the composites. Hence, the density of SiC-based composite increased with the existence of Si3N2O. In addition, the formation of Si3N2O was desirable because this phase conferred the excellent high temperature strength and oxidation

\[\text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{N}_2\text{O}\]
resistance [28-29]. Furthermore, the typical hot pressing temperature of >1800 °C for Si₃N₄/SiC composites can be used to achieve the density of >3.00 g/cm³ with the addition of 8-15 wt. % sintering additives [13,30-32], which was higher compared to this study.

SEM images of the fractured surface of HEM1600, HEM1700, 1600 and 1700 are shown in Figure 4. Since no other phase such Si₃N₄O and ZrO₂ was found, the microstructure of 1600 (Figure 4 (c)) was very fine, and the grain size cannot be seen clearly with SEM. However, at 1700 (Figure 4 (d)), the grain grew tremendously without densification mechanism, resulting in density of only 2.47 g/cm³ corresponding to 76.9% relative density (theoretical density of SiC = 3.21 g/cm³). On the other hand, SiC-based composite with dense microstructure was obtained at 1700 °C as seen in Figure 4 (b).

Although there was a grain growth in HEM1700 (Figure 4 (b)) compared to HEM1600 (Figure 4 (a)), the growth was not significant compared to 1700 (Figure 4 (d)), which meant that the densification mechanism took place in the sintering of milled amorphous Si-C-N-O as described before. The mean grain sizes for HEM1700 (Figure 4 (e)) was 293 nm, much finer than the typical grain size of submicron/micrometer with the conventional method [11,21-23]. Fine microstructure of HEM1700 was formed probably due to the high viscosity in liquid phase of Si₃N₄O. This result is in agreement with the sintering of SiC with the addition of AlN, whereas the liquid phase containing N₂ had higher viscosity [33]. Three phases were observed in the SEM image of Figure 4 (f); black, grey, and white. Energy dispersive X-ray spectroscopy analysis revealed that the grey and white phases were SiC and ZrO₂, respectively, while the black area was Si₃N₄ and Si₂N₂O.

4. Conclusions

High density SiC-based composites from polysilazane were successfully prepared by high energy milling without the addition of sintering additives. The density of 3.04 g/cm³ could be achieved by 1 hour hot pressing at 1700 °C under an applied pressure of 50 MPa in
vacuum atmosphere for HEM1700, while 2.47 g/cm$^3$ for 1700. The formation of Si$_3$N$_2$O that involved liquid phase in amorphous Si-C-N-O was imperative to achieve high density SiC-based composites from polysilazane. Moreover, the presence of Si$_3$N$_2$O played an important role in restraining the grain growth of the composites.

References